



# CHALMERS

## Chalmers Publication Library

### **Gas Phase Alkali Chlorides and Deposits during Co-Combustion of Coal and Biomass**

This document has been downloaded from Chalmers Publication Library (CPL). It is the author's version of a work that was accepted for publication in:

**Proceedings 19th FBC Conference from May 21 -May 24 2006 in Vienna/AUSTRIA**

Citation for the published paper:

Kassman, H. ; Andersson, C. ; Högberg, J. et al. (2006) "Gas Phase Alkali Chlorides and Deposits during Co-Combustion of Coal and Biomass". Proceedings 19th FBC Conference from May 21 -May 24 2006 in Vienna/AUSTRIA

Downloaded from: <http://publications.lib.chalmers.se/publication/237950>

Notice: Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source. Please note that access to the published version might require a subscription.

Chalmers Publication Library (CPL) offers the possibility of retrieving research publications produced at Chalmers University of Technology. It covers all types of publications: articles, dissertations, licentiate theses, masters theses, conference papers, reports etc. Since 2006 it is the official tool for Chalmers official publication statistics. To ensure that Chalmers research results are disseminated as widely as possible, an Open Access Policy has been adopted. The CPL service is administrated and maintained by Chalmers Library.

(article starts on next page)

# PROCEEDINGS

## 19<sup>th</sup> FBC Conference

from May 21 – May 24 2006

in

Vienna / AUSTRIA



## Part II

# Gas Phase Alkali Chlorides and Deposits during Co-Combustion of Coal and Biomass

*H. Kassman*<sup>1</sup>, *C. Andersson*<sup>2</sup>, *J. Högberg*<sup>2</sup>, *L.-E. Åmand*<sup>3</sup> and *K. Davidsson*<sup>3</sup>

<sup>1</sup>Corresponding author: [hakan.kassman@vattenfall.com](mailto:hakan.kassman@vattenfall.com)

Vattenfall Power Consultant AB, P.O. Box 1046, SE 611 29 Nyköping, Sweden

<sup>2</sup>Vattenfall Utveckling AB, SE 814 26 Älvkarleby, Sweden

<sup>3</sup>Department of Energy and Environment, Division of Energy Technology, Chalmers University of Technology, SE 412 96 Göteborg

## Abstract

Straw pellets have been co-fired with a bituminous coal with a high chlorine content. The tests were carried out in a 12 MW circulating fluidized bed (CFB) boiler located at Chalmers University of Technology in Sweden. The tests focused on variation of the ratio of straw to coal in combination with different feeding rates of limestone to the bed. Three test series were carried out: Lime – the fuel was a constant mixture of coal and straw pellets, with an increasing lime supply; Coal – the fuel was coal only, with an increasing lime supply. Alkali – the fuel was coal and straw pellets and constant lime supply. The fraction of straw pellets (alkali) was increased.

An *In-situ* Alkali Chloride Monitor (IACM) was used during the tests to measure the on-line concentration of alkali chlorides and SO<sub>2</sub> before the convection section of the boiler. Deposit measurements were also carried out and the deposits were analysed by means of SEM-EDX. It was found that an increased fraction of straw pellets in the fuel mix results in increased level of alkali chlorides in the gas phase as well as in collected deposits.

## Introduction

Co-combustion of biomass with coal or other primary fuels has many potential advantages: the effective emission of CO<sub>2</sub> is reduced by replacing a certain amount of coal with biomass, and efficient utilisation of the energy in biomass by converting it to electricity in a coal power station. There are also potential risks: some biofuels may lead to deposit formation on heat exchanger surfaces in the combustor or to bed agglomeration in a fluidised bed. Fluidised bed combustion is probably the most advantageous method available for co-combustion due to its fuel flexibility and the possibility to influence the processes of formation and destruction of emissions.

There are several important factors to investigate when co-firing coal and biomass. This project focuses on the possibility of co-firing a troublesome fuel (with respect to alkali related problems) such as straw with coal. Gas phase alkali chlorides was measured by means of an *In-situ* Alkali Chloride Monitor (IACM) and SEM-EDX was used for analysis of collected deposit. IACM was also used as a tool for on-line judgements of the limits of co-firing in order to avoid deposit problems. The results from SEM-EDX analysis were used to support the results from IACM. The results were also discussed with respect to mechanisms that could explain the positive

synergy effect of co-firing coal with alkali rich biofuels. Three test series were carried out with variation of the ratio of straw pellets to coal in combination with different feeding rates of limestone to the bed. Straw pellets were used as an alkali source and their potential in producing deposits is demonstrated in ref. [1]. The results from co-combustion of a chlorine rich coal and an alkali rich biomass such as straw pellets could also be relevant to co-combustion of waste. A similar situation occurs during co-combustion of a low chlorine coal and a chlorine rich waste such as PVC together with an alkali rich biomass.

## Experimental

### *The boiler and the operating conditions*

The 12 MW CFB boiler at Chalmers University of Technology (CTH) was used for the experimental runs. The device resembles in principle the scheme shown in Fig. 1. The combustion chamber of the Chalmers boiler (1) has a square cross-section of about 2.25 m<sup>2</sup> and a height of 13.6 m. Fuel is fed from the bottom. The circulating bed material is recirculated through a cyclone (2) back to the combustion chamber, whereas the combustion gases enter the “convection path” where the gases are cooled down to 150 °C before cleaning in a secondary cyclone and a bag filter. The measurements of gas concentrations and deposits were carried out in a location just before the convection path starts.

The different fuel properties are given in Table 1. The base fuel was a high chlorine containing Polish bituminous coal. Straw pellets from Denmark were used as additional fuel in all tests with a constant ratio of about 20% of the energy content. A reference case without coal as fuel was also run for comparison. During this reference case, a mixture of wood pellets and wood chips was used as base fuel instead of coal, and chlorine was added as PVC (norvinyl S7060 from Hydro Polymers, Sweden) in order to compensate for the chlorine in the coal. The chlorine content in straw pellets is 60 times higher than in wood pellets and wood chips (Table 1). The potassium (K) content on ash basis is about the same as the two other biofuels. However, since the ash content is about 16 times higher, the loading of K increases using straw as additional fuel to coal, compared to the more cleaner wood pellets or wood chips. The potassium in wood probably forms KCl with the chlorine contained in both the straw and the coal according to previous experience. [2]. The operating conditions typical for the CFB boiler during the test series are presented in Table 2 (average and standard deviation). As starting bed material silica sand (dp=0.3 mm) was used. By using coal and lime addition the silica sand bed was gradually replaced by coal ash and lime.

### The test series

Tables 3 and 4 outline the main features of the reference and the three test series. Each test series has three to four operating cases. The reference and the test series can be summarised as follows:

- Reference – no coal or lime, the fuel was a mixture of wood chips, wood pellets and straw pellets. In order to compensate for the chlorine content in the coal and raise the Cl/(K+Na) ratio, PVC was also added in this test.
- Lime, (tests A0-A3) – the fuel was a constant mixture of coal and straw pellets, with an increasing lime supply (Ignaberga limestone, dp=0.2-2 mm).
- Coal, (tests B1-B3) – the fuel was coal only, with an increasing lime supply.
- Alkali, (tests C1-C3) – the fuel was coal and straw pellets and a constant lime supply (Ca/S molar ratio). The fraction of straw pellets was increased (increased alkali supply).

The molar ratios, presented in Tables 3 and 4 are calculated (based on fuel analysis) according to various references [3]-[8] discussing alkali related fouling and/or corrosion in the superheater region. The relevance of these molar ratios will be discussed later in the paper. The changing parameters in each test series are shown in bold.

Table 1. Fuel properties

	Bituminous coal	Straw pellets	Wood pellets	Wood chips
<b>Proximate analysis</b>				
Water (wt-%, raw)	9.6	11.3	7.7	42.4
Ash (wt-%, dry)	9.8	6.9	0.3	0.6
Combustibles (wt-%, dry)	90.2	93.1	99.7	99.4
Volatiles (wt-%, daf)	34.1	80.7	81.6	83.4
<b>Ultimate analysis (wt-%, daf)</b>				
C	81.7	49.1	50.3	49.9
H	4.8	6.3	6.2	6.2
O	11.1	43.4	43.4	43.8
S	6.23	0.12	0.01	0.02
N	1.45	0.73	0.05	0.15
Cl	0.32	0.36	0.01	0.01
<b>Ash analysis (g/kg dry ash)</b>				
K	13	110	92	120
Na	13	9.0	4.8	4.9
Al	81	6.5	7.7	3.7
Si	210	300	43	18
Fe	60	2.1	18	2.0
Ca	73	52	210	230
Mg	38	10	31	36
P	1.7	14	12	17
Ti	3.7	0.4	0.3	0.2
Ba	1.4	0.4	4.0	0.9
<b>Lower heating value (MJ/kg)</b>				
Hu, daf	31.92	18.42	18.89	18.63
Hu, raw	25.79	14.93	17.19	9.61

daf= dry and ash free, raw= as received

Table 2. Operating conditions for the tests

	Average	S-dev.
load, MW <sub>th</sub>	6.1	0.1
bed temp., °C (bottom)	850	1
bed temp., °C (top)	865	3
exit temp. of after burning chamber, °C	828	6
total riser pressure drop, kPa	7.6	0.2
primary air flow/total air flow, %	44	4
superficial flue gas velocity at top of riser U <sub>top</sub> , m/s	4.8	0.2

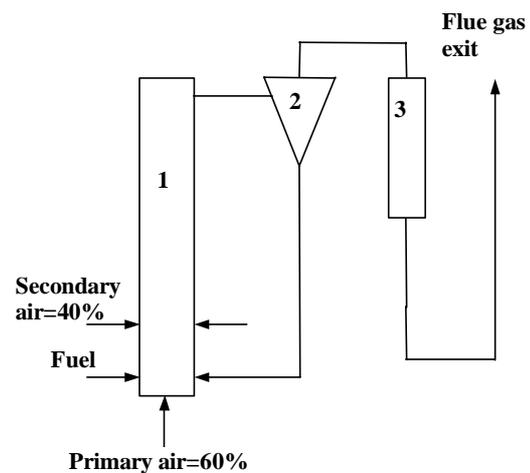


Fig. 1. CFB combustor. 1 Combustion chamber, 2 Particle separator, cyclone, 3 Convection path.

Table 3. Molar ratios during reference and test series A (increasing lime supply)

Test series	No coal <sup>(1)</sup>	Lime <sup>(2)</sup>	Lime <sup>(2)</sup>	Lime <sup>(2)</sup>	Lime <sup>(2)</sup>
Operating case	Reference	A0	A1	A2	A3
Fraction of straw <sup>(3)</sup> , %	14	17.2	18.7	16.8	17.0
2*S/(K+Na) molar ratio	0.4	2.3	2.2	2.3	2.3
S/(Ca+K <sub>2</sub> +Na <sub>2</sub> ) molar ratio	0.07	0.35	0.34	0.19	0.12
S/Cl molar ratio	0.14	1.6	1.6	1.7	1.6
Cl/(K+Na) molar ratio	1.4	0.72	0.68	0.69	0.72
(Al+Si)/(fuel Cl) molar ratio	14	13	13	12	11
Ca addition molar ratio Ca/S	0	<b>0</b>	<b>0</b>	<b>2.5</b>	<b>5.7</b>
Ca/S with Ca in fuel included	4.4	1.1	1.1	3.6	6.8
Desulphurization (%)	59.5	48.5	62.6	90.3	98.9

(1)= Mixture of wood pellets, wood chips, straw pellets and PVC, no lime supply. (2)= straw pellets + coal, increasing lime supply. (3)= energy basis,

Table 4. Molar ratios during test series B (coal only, increasing lime supply) and test series C (increasing alkali supply)

Test series	Coal <sup>(1)</sup>	Coal <sup>(1)</sup>	Coal <sup>(1)</sup>	Alkali <sup>(2)</sup>	Alkali <sup>(2)</sup>	Alkali <sup>(2)</sup>
Operating case	B1	B2	B3	C1	C2 <sup>(4)</sup>	C3
Fraction of straw <sup>(3)</sup> , %	0	0	0	<b>8.8</b>	<b>17.0</b>	<b>29.1</b>
2*S/(K+Na) molar ratio	4.0	4.0	4.0	2.9	2.3	1.7
S/(Ca+K <sub>2</sub> +Na <sub>2</sub> ) molar ratio	0.49	0.23	0.15	0.14	0.12	0.10
S/Cl molar ratio	2.2	2.2	2.2	1.9	1.6	1.0
Cl/(K+Na) molar ratio	0.9	0.92	0.92	0.78	0.72	0.9
(Al+Si)/(fuel Cl) molar ratio	13	13	13	12	11	13
Ca addition molar ratio Ca/S	0.0	2.3	4.9	4.9	5.7	6.2
Ca/S with Ca in fuel included	<b>1.0</b>	<b>3.3</b>	<b>5.9</b>	6.0	6.8	7.4
Desulphurization (%)	53.5	85.6	98.8	99.4	98.9	99.9

(1)= coal only (no alkali supply), increasing lime supply. (2) straw pellets + coal, lime supply constant, increasing straw (alkali) supply. (3)= energy basis, (4)= same test as Lime A3

### Measurement techniques

Alkali chlorides exist in the gas phase when the flue gas temperature is greater than 650°C. Vattenfall has developed and patented an instrument for *in-situ* measurement of gaseous alkali chlorides [9]. This instrument, an *In-situ* Alkali Chloride Monitor (IACM) [10]-[12], measures the sum of the sodium and potassium chloride concentrations on-line but it can not distinguish between these two species. IACM is also able to measure sulphur dioxide at the same time. Light from a xenon lamp is sent across the furnace or flue gas channel by a couple of optical units. The light, which arrives at the receiver, is analysed by a spectrometer. The measurements are made by the principle of optical absorption. Since alkali chlorides (and other gas molecules) absorb light at certain characteristic wavelengths, the level of alkali chloride in the spectrum can be determined. IACM uses light in the wavelength range of 200-380 nm for the analysis of KCl and NaCl, and SO<sub>2</sub>. The instrument has a sampling time of 5-10 seconds. The detection limit at a 5 metre measuring length (width of the flue gas channel) is 1 ppm for KCl and NaCl and 4 ppm for SO<sub>2</sub>.

Flue gas was extracted through a heated probe and heated sampling lines to a FTIR (Fourier transform infra-red) analyser for the determination of HCl and SO<sub>2</sub> on hot wet flue gases and further to an on-line IR-VIS instrument measuring SO<sub>2</sub> on cold dry gases. These measurements were carried out in a sampling location next to the IACM instrument.

The initial deposits were collected on steel rings during a period of four hours using a temperature controlled probe held at 500°C. The deposit rings were stored in a dry environment and analysed by means of a Scanning Electron Microscopy instrument equipped with energy dispersive X-ray fluorescence detector (SEM-EDX). The

deposits were analysed for elements on the wind side, lee side and at an angle of 50 degree from the wind side which is the same procedure as in other studies of deposits [13], [14].

## Results

The level of alkali chlorides measured by IACM is expressed as KCl and recalculated on dry basis to an oxygen concentration of 6 %.

### *IACM*

Fig. 2 shows the results from the operating cases during test series “Coal” when only coal was used as fuel with an increasing lime supply. The KCl level is generally very low and independent of the concentrations of SO<sub>2</sub>. The measured level of SO<sub>2</sub> is somewhat higher using FTIR compared to IACM and conventional IR. This deviation for FTIR could be explained by limitations in the calibration range. SO<sub>2</sub> decreases as expected due to increasing Ca/S ratio. The HCl level is high and decreases somewhat by the increasing lime supply. The dotted line shows that the level of KCl was about 70 ppm during the reference case with no coal.

Fig. 3 shows the results from the operating cases during test series “Lime”, during co-combustion of coal and straw pellets with an increasing lime supply. The alkali supply was equal to a fraction of straw of 17-19% on energy basis. Adding straw pellets to the fuel mixture with sufficient amounts of chlorine available increased the KCl with approximately one order of magnitude (from ~2 to ~20ppm). Still the level of KCl seems to be independent of the SO<sub>2</sub> concentration. This is a somewhat unexpected result since sulphur is known to promote the formation of K<sub>2</sub>SO<sub>4</sub> (potassium sulphate).

Fig. 4 shows the results from the operating cases during test series “Alkali”, during co-combustion of coal and straw pellets with a constant lime supply and an increasing ratio of straw pellets. The lime supply was equal to a Ca/S ratio of 6.2-6.9 (including the Ca in fuel ash). KCl starts to increase during increased straw pellets ratio. For the test corresponding to a straw fraction of 29% (on energy basis) a level of 50 ppm KCl was achieved. This level is believed to be much too high with respect to potential problems with fouling and superheater corrosion [12]. IACM could, consequently, be used for on-line measurement of KCl and too high concentrations could be avoided by controlling the fraction of straw pellets in the in-coming fuel mix.

### *SEM-EDX*

The results from the SEM-EDX analysis of the deposit rings are shown in Figs. 5-10. Only elements important for the deposit chemistry are included in the figures, (Cl, Na, K, Al, Si, S and Ca). All three positions (wind side, 50° angle from wind and lee side) are presented for the test series “Lime”. The results of the wind side are very similar to those at 50° angle from wind (Fig. 5 compared to Fig. 6 and Fig. 8 compared to Fig. 9). The element concentrations are, in general, lower on the lee side compared to the two other positions. This could be explained by the fact that the deposit layer on the lee side after only 4 hours of exposure is rather thin making SEM-EDX analysis uncertain. In all of the Figs. 5-10, the bar charts for the so-called reference case with no coal and no lime are presented in contrast to the other test series with coal. The reference case deviates significantly in these figures and especially with respect to:

- a) higher concentrations of K and Cl in the deposits. This occurs at the same time as high concentrations of KCl are measured with IACM, (indicated by dotted lines in Figs 2 to 4). Increased KCl in the flue gas correlates with higher levels of K and Cl in the deposits during biomass combustion.
- b) lower concentration of Al. Relatively high concentrations of both Al and Si were detected when coal was used but during the reference case only some Si was found. Coal ash contains high concentrations of both Al and Si, while straw pellets contain high concentrations of Si only compared to wood pellets and wood chips, Table 1. These observations are important for the interpretation of the alkali capture behaviour discussed later.

Other observations from a study of the SEM-EDX results are:

- a) In test series “Coal”, the increase of lime supply is seen as a gradually increased Ca content in the deposits. This is expected and at the same time K, Al and Si decreased. The content of sulphur (S) in the deposits is higher in B2 compared to B1, and at the same time has SO<sub>2</sub> in the flue gas decreased. B3 represents a case with an excess of lime and the increase of Ca is not followed by an increase in S in the deposits (Figs. 8-9) since there is almost no remaining S to capture going from B2 to B3, (Fig 2). There was no Cl in the deposits when lime was not supplied (test B1, Figs. 8-9). Very low Cl concentrations were still measured in the deposit during addition of normal amounts of lime (B2). However, the excess supply of lime (B3) leads to a slight decrease in HCl (Fig. 2) followed by a significant increase of Cl in the deposit. This interesting observation is most probably linked to the capture of Cl by lime forming calcium chloride (CaCl<sub>2</sub>). This reaction was suggested in [8] for similar tests burning coal and meat and bone meal with an excess of lime in a pilot scale CFB.
- b) In test series “Lime”, where straw pellets were co-fired at a constant ratio with increased lime supply, Cl was present in all the deposits. The Cl concentrations are low for cases A0 and A1 (Figs. 5, 6) but both cases with increased lime (A2, A3) led to increasing Cl. It was, nevertheless, not even close to the conditions prevailing for the reference case without coal. The HCl concentration decreased with increasing lime supply in a similar way as already observed in test series B (Fig. 3 compared to Fig. 2). The increase of Cl in the deposits could also be explained here by the formation of CaCl<sub>2</sub>.
- c) In test series “Alkali” with an increasing ratio of straw pellets during an excess supply of lime, significant amounts of both Cl and K were found in the deposits, Fig. 10. A lower fraction of straw (C1) led to the lowest concentrations of both Cl and K. Nevertheless, by increasing the ratio of straw pellets Cl in the deposits increased drastically. This correlates well to the increased KCl in Fig. 4. The present SEM-EDX analysis does not specify if Cl in the deposits is due to capture of Cl as CaCl<sub>2</sub> or as KCl. Further spot analysis that reveals how the elements are associated to each other could possibly clarify this and also explain how the potassium is bound.

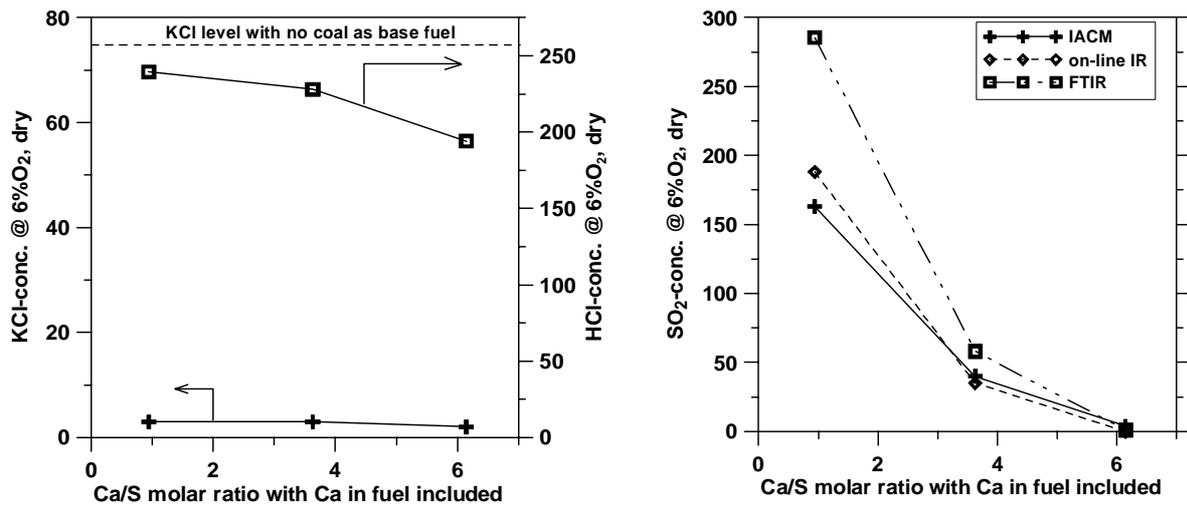


Fig. 2 Concentrations of KCl, HCl (left) and SO<sub>2</sub> (right) before the convection pass for the test series “Coal” with only coal as fuel. Note the dotted line which is KCl for the reference without coal as fuel (straw- wood pellets and wood chips). The HCl level for this case was 132 ppm.

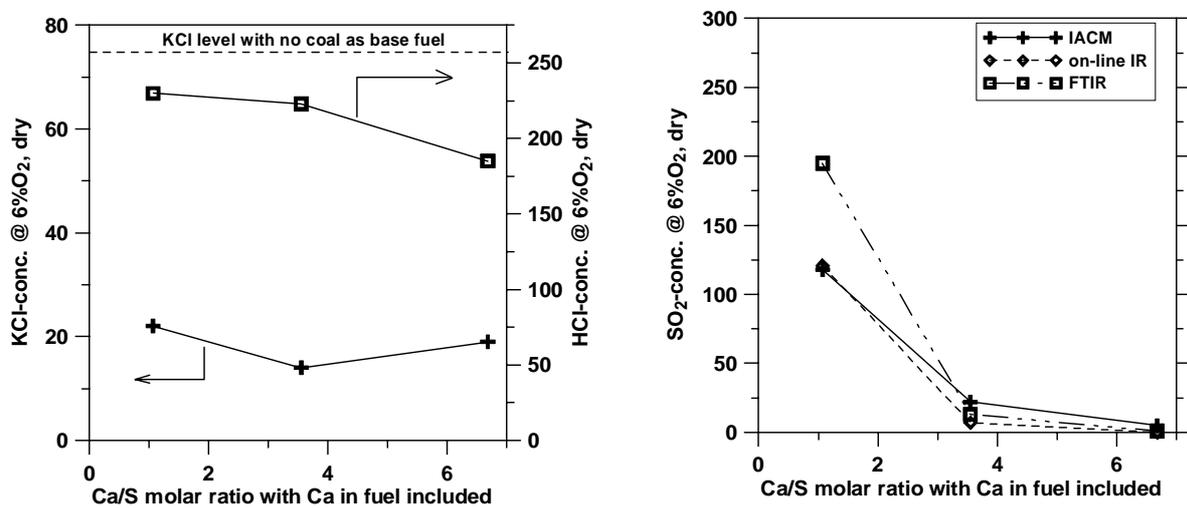


Fig. 3. Concentrations of KCl, HCl (left) and SO<sub>2</sub> (right) before the convection pass for the test series “Lime” with co-combustion of straw pellets with coal and increasing lime supply. Note the dotted line which is KCl for the reference without coal as fuel (straw- wood pellets and wood chips). HCl for this case was 132 ppm.

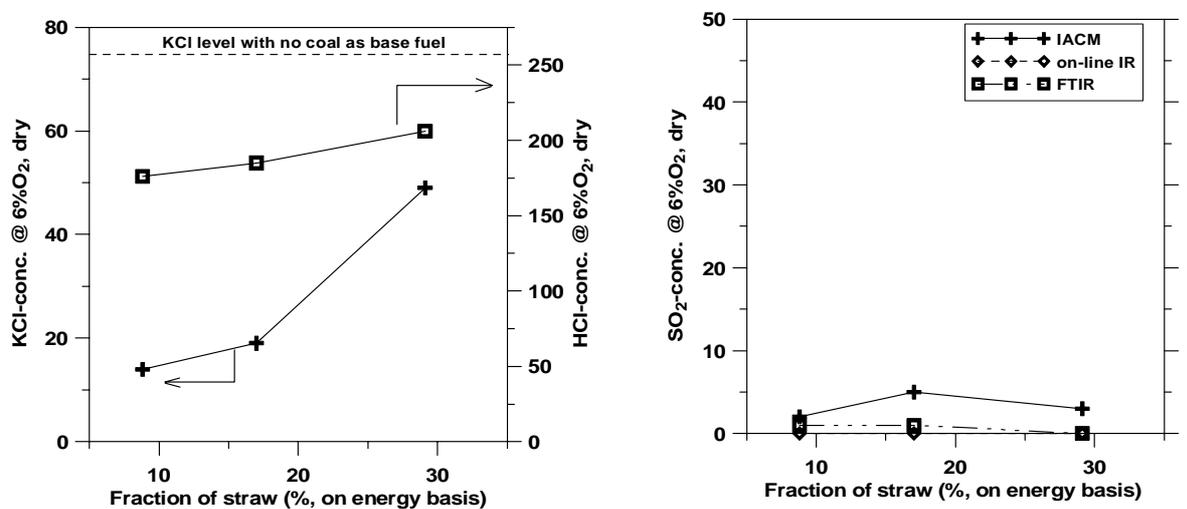
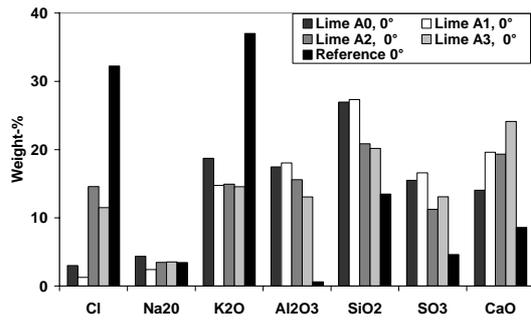
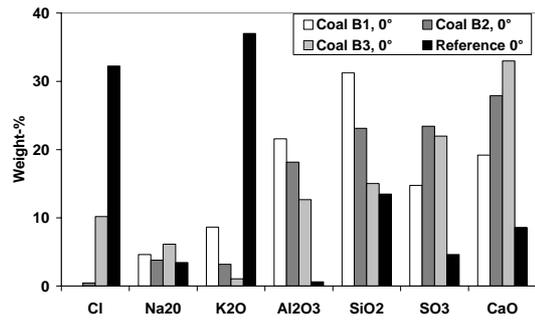


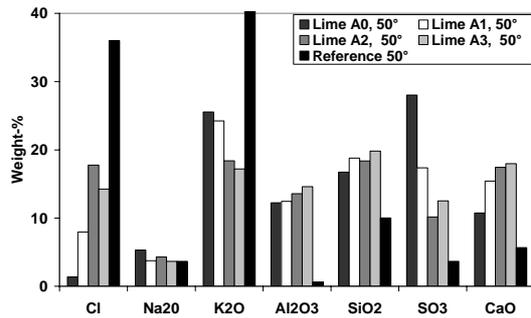
Fig. 4. Concentrations of KCl, HCl (left) and SO<sub>2</sub> (right) before the convection pass for the test series “Alkali” with co-combustion of straw pellets with coal and increasing alkali supply. Note the dotted line which is KCl for the reference without coal as fuel (straw- wood pellets and wood chips). HCl for this case was 132 ppm.



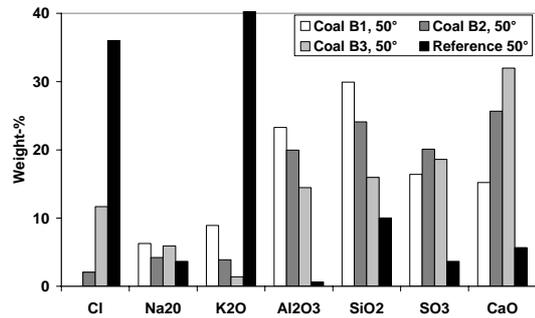
**Fig. 5.** Test series “Lime” - Deposits analysed by SEM-EDX at the wind side 0°.



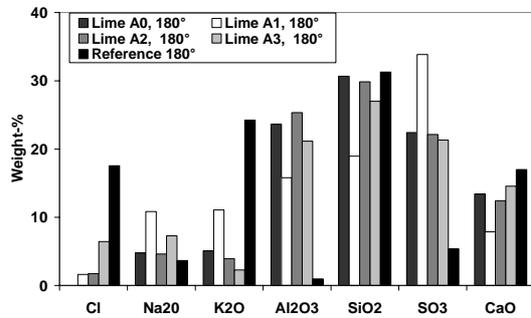
**Fig. 8.** Test series “Coal” - Deposits analysed by SEM-EDX at the wind side 0°.



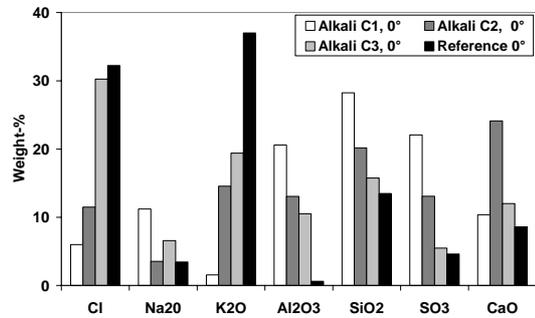
**Fig. 6.** Test series “Lime” - Deposits analysed by SEM-EDX at an angle of 50° from the wind side.



**Fig. 9.** Test series “Coal” - Deposits analysed by SEM-EDX at an angle of 50° from the wind side.



**Fig. 7.** Test series “Lime” - Deposits analysed by SEM-EDX at the lee ward side 180°.



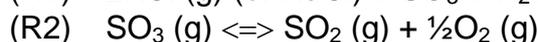
**Fig. 10.** Test series “Alkali” - Deposits analysed by SEM-EDX at the wind side 0°.

## Discussion

The literature suggests two explanations for the positive synergy effect of co-firing coal with an alkali rich biofuel such as straw. These are sulphation of the alkali chlorides and chemical reaction between the components in the coal ash and alkali.

### Sulphation

Sulphation of the alkali chlorides by reaction R1 and R2 can occur if sulphur is present.  $\text{SO}_3$  is in equilibrium with  $\text{SO}_2$  and  $\text{SO}_3$  is favoured by oxidising conditions (R2) The sulphation rate in gas phase is fast and limited by the availability of  $\text{SO}_3$  [13].

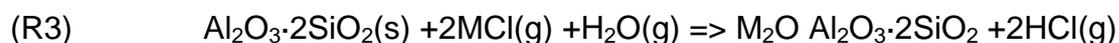


This sulphur can originate from the fuel or from additives such as elemental sulphur or ammonium sulphate. Deposits containing sulphates are less harmful than chlorides. The formation of deposits also decreases due to the tendency of  $K_2SO_4$  to condensate and form aerosol particles in the gas.  $K_2SO_4(s)$  is thereby less inclined to stick to the tube surfaces. It has been proposed by Krause [3] that when the molar ratio of S/Cl in the fuel is greater than four, corrosion caused by chlorine is negligible. In the present tests, this ratio is 2.2 for the coal only but decreases to 1.9-1.0 using straw as additional fuel depending on the fraction of straw, Table 4. Similarly, Robinson et al. [4] stated that when the molar ratio  $2S/(K+Na) > 4$ , the Cl content in deposits is negligible. The term (K+Na) expresses the amount of so-called *available* alkali in the mineral part of the fuel, thus excluding alkali firmly bound in minerals. Using fuel alkali instead of *available* alkali, this relation was 4 for test series B (coal) and between 2.9 and 1.7 for test series C (straw), Table 4. It is a well known fact that this is a simplified concept and that several complications have to be considered when relating these molar ratios to deposits (Yrjas et al. [6]; Silvennoinen et al. [7]).

Leaching tests showed that alkali in wood is almost entirely free to be released (Yrjas et al. [6]), whereas alkali in coal is to a great extent, bound in the ashes. Thus in the cases with coal, the  $2S/(K+Na)$  ratio given in Table 4 is increased to higher values than those given in the table, and then the criteria are fulfilled as long as the sulphur is not removed by additional sorbents like lime. This is, however, what happened in all test cases either with Ca bound in the ash or by added Ca. Yrjas et al. [6] introduced the ratio  $S/(Ca+K_2+Na_2)_{reactive}$  in order to account for the lime effect. Here a ratio of one means that there is sufficient S available for sulphation of all Ca, K and Na present. For the tests in this paper, most of the alkali is available, whereas most of the Ca is added. For test series B (coal), the ratio is in the range of 0.40 to 0.15, Table 4. The corresponding range is 0.35-0.12 for test series "Lime", Table 3 while test series "Alkali" gave 0.14-0.10. The lime supply thus creates a lack of S as was intended and also confirmed by the on-line measurements of  $SO_2$ , Figs. 2-4.

#### *Ash reactions*

Chemical reactions between the components of the coal ash, particularly aluminosilicates, and potassium (or sodium), liberating chlorine in gaseous form (HCl) and binding the potassium (or sodium) in the ashes occur according to the overall reaction (R3).



The reactions between sodium (which is rather similar to potassium) and kaolinite was found to be faster for NaOH than for NaCl, Mwabe and Wendt [14], whereas Tran et al. [15] found no difference in reaction rate for KOH and KCl and kaolin under combustion conditions (850 °C and water vapour present). For the present tests, any of the potassium compounds mentioned above could have been present initially and reacted with aluminosilicates even before  $K_2SO_4$  was formed. Here it is sufficient to state that this is a likely process. Aho and co-workers [7], [8], [16] have suggested that aluminosilicates are important for binding potassium from biomass combustion in connection to co-combustion of coal and other fuels. Aho and Silvennoinen [16] have suggested that a molar ratio of reactive (Al+Si)/Cl higher than 8 to 10 was required to prevent chlorine in deposits. In Tables 3 and 4, the values for the corresponding molar ratios are given for the present tests and high ratios are

achieved for all test series including the reference case with no coal. The ratio is misleading for that case since the high value is achieved due to the Si content of the straw and this is not an indication of the presence of alumino-silicates rather the presence of silica that does not capture alkali according to (R3). In a project carried out in the same boiler as the present tests, sewage sludge was co-fired with wood, spiked with chlorine (in the form of HCl), [17]. The sludge that contains zeolites (a natural form of alumino-silicates) as part of the ash is in that paper discussed to take part in the capture of the alkali chlorides.

#### *Co-combustion of coal and biomass*

The KCl level is about 70 ppm during the reference case with no coal. This means that a reduction from 70 to approximately 20 ppm has occurred in the three cases in Fig. 3. This could be due to reaction of KCl with sulphur (R1 and R2) parallel to the sulphur capture reaction with lime or that some component of the coal ash reacts with KCl (such as in R3) independently of the sulphur reaction with KCl. The latter reaction is supported by the SEM-EDX analysis of the deposits and the high concentrations of Al and Si in all deposits when coal is used. This result (high Al and Si content in the deposits) has proved very similar to that achieved in [8] where coal was used with meat and bone meal, in [7] where coal was used with a chlorine containing waste (RDF) or demolition wood and in [16] where pine bark was used either with a deinking sludge from the pulp & paper industry (containing kaolinite) or with addition of kaolinite to the CFB test rig.

It is not possible to determine the most important of the mechanisms (sulphation of KCl in parallel to reaction of Ca with S or reaction with ash components). Nevertheless, test series "Alkali" where the ratio of straw was gradually increased supports reaction R3 with ash components of the coal. During these tests, an excess of lime was used in order to keep the SO<sub>2</sub> concentration out from the boiler as close as possible to zero. Still the coal ash might be active in reacting with KCl but by increasing the straw pellets ratio a break through of KCl is clearly seen. This can be interpreted as a gradually lack of alumino-silicates. The molar ratios (Al+Si)/(fuel Cl) using coal are also much more favourable than the ratio  $S/(Ca+K_2+Na_2)_{\text{reactive}}$  where the sulphur capture by lime is considered. As shown in [7] and [8] different coal types have greatly varying efficiency with respect to reaction R3. This is probably due to differences in the content of kaolinite in the coal ash. In most investigations, this is discovered after the tests when the deposits have been analysed. In the present tests, IACM was proven to be a powerful tool for the on-line judgement of the level of alkali chlorides in the boiler. In practical operation, this could be very valuable during co-combustion of coal with a fuel containing significant levels of available alkali. IACM could be used for selection of a proper ratio between the base fuel coal and the additional fuel (a biomass such as straw and/or waste). IACM becomes even more useful firing a high chlorine containing coal or if the fuel mix also consists of a chlorine containing waste such as RDF.

## Conclusion

The results for three test series can be summarised as follows:

- KCl was close to the detection limit (~2 ppm) during combustion of coal independent of lime supply. The alkali in the coal ash is thus not released to form alkali chlorides, so-called *available* alkali.
- Co-combustion of coal with straw pellets that released *available* alkali, increased KCl to approximately 20 ppm. No clear relationship was seen between increased lime supply and KCl.
- High concentrations of Al and Si were found in the deposits during SEM-EDX analysis for all tests using coal. This is an indication of the presence of alumino-silicates that can capture the alkali and thus prevent the formation of alkali chlorides.
- The removal of SO<sub>2</sub> by excess amounts of lime, in combination with increased amounts of *available* alkali, leads to an increase of KCl from 15 to 50 ppm despite the presence of reactive coal ash.
- It was possible to measure the alkali chlorides (KCl) on-line by means of IACM. An IACM can be used for on-line fuel quality control in order to avoid operational problems during co-combustion of coal and biomass.
- Excess supply of lime probably leads to the capture of Cl forming CaCl<sub>2</sub>.

## References

1. Nielsen, H.P., Baxter, L.L., Sclippab, G., Morey, C., Frandsen, F.J., Dam-Johansen, K., "*Deposition of Potassium Salts on Heat Transfer Surfaces in Straw-Fired Boilers: a Pilot Study*", Fuel, vol. 79, pp. 131-139, 2000.
2. Miettinen Westberg H., Byström M. and Leckner B., "*Distribution of Potassium, Chlorine, and Sulfur between Solid and Vapor Phases during Combustion of Wood Chips and Coal*", Energy & Fuels, vol 17, pp. 18-28, 2003.
3. Krause, H.H., "*High-temperature corrosion problems in waste incineration systems*", J. Materials for Energy Systems, vol 7, pp. 322-332, 1986.
4. Robinson, A.L., Junker, H., Baxter, L.L., "*Pilot scale investigation of the influence of coal-biomass cofiring on ash deposition*", Energy & Fuels, vol. 16, pp. 343-355, 2002.
5. Salmenoja, K., "*Field and laboratory studies on chloride induced superheater corrosion in boilers fired with biofuels*", Ph.D thesis, Faculty of chemical engineering, Åbo Akademi University, Turku, pp. 102, 2001.
6. Yrjas P., Skrifvars B.-J., Hupa M., Roppo J., Nylund M. and Vainikka P., "*Chlorine in deposits during co-firing of biomass, peat, and coal in a full-scale CFBC boiler*", Proceedings of the 18<sup>th</sup> International Conference on Fluidized Bed Combustion, paper FBC2005-78097, The American Society of Mechanical Engineers, Toronto, Canada, 2005.
7. Silvennoinen, J., Roppo, J., Nurminen, R.-K., Aho, M., Vainikka, P., Ferrer, E., "*Co-Combustion of Coal with RDF and Biomass – Prevention of Chlorine Deposition by Using Coal Ash Alkali Absorption Ability*", Proceedings of the 18<sup>th</sup> International Conference on Fluidized Bed Combustion, paper FBC2005-78120, The American Society of Mechanical Engineers, Toronto, Canada, 2005.

8. Aho, M., Ferrer, E., "Importance of Coal Ash Composition in Protecting the boiler Against Chlorine Deposition During Combustion of Chlorine-Rich Biomass", *Fuel*, vol. 84, pp 201-212, 2005.
9. IACM. Swedish Patent SE 9903656-8, (2001). International Patent application PCT/SE 00/01866, 2000.
10. Henderson, P., Andersson, C., Kassman, H., Högberg, J., *Reducing superheater corrosion in wood-fired power plant*. Proc Conf. BALTICA VI "Life Management and Maintenance for Power Plants" VTT Symposium 233, pp. 143-154, 2004.
11. Henderson, P., Andersson, C., Kassman, H., "The Use of Fuel Additives in Wood and Waste Wood-fired Boilers to Reduce Corrosion and Fouling Problems", *VGB PowerTech*, vol 6, pp. 58-62, 2004.
12. Henderson, P., Kassman, H., Andersson, C., *The use of Ammonium Sulphate in Waste-Fired Boilers to reduce Superheater Fouling and Corrosion and NOx emissions* Proc Swedish Finnish Flame days, Borås, Sweden, 2005.
13. Iisa, K., Lu, Y., Salmenoja, K., "Sulfation of Potassium Chloride at Combustion Conditions". *Energy & Fuels*, 13, pp. 1184-1190, 1999.
14. Mwabe P.O., Wendt J.O.L., "Mechanisms Governing Trace Sodium Capture by Kaolinite in a Downflow Combustor", In: Proc. 26th Symp. (Int.) on Combustion, Pittsburgh, The Combustion Institute, pp. 2447-2453, 1996.
15. Tran K.-Q., Iisa K., Steenari B.-M., Lindquist O., "A Kinetic Study of Gaseous Alkali Capture by Kaolin in the Fixed Bed Reactor Equipped With an Alkali Detector", *Fuel*, vol. 84, pp.169-175, 2005.
16. Aho M., Silvennoinen J., "Preventing Chlorine Deposition on Heat Transfer Surfaces with Aluminium–Silicon Rich Biomass Residue and Additive", *Fuel*, vol. 83, pp. 1299-1305, 2005.
17. Åmand L.-E., Leckner B., Eskilsson D., Tullin C., "Deposits on Heat Transfer Tubes During Co-Combustion of Biofuels and Sewage Sludge", Article in press for publication in *Fuel*, <http://www.fuelfirst.com>, 2006.